CORNING

ULE® Glass with Improved Thermal Properties for EUVL Masks and Projection Optics Substrates

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Introduction – Ultra Low Expansion ULE® Glass

- Corning has made ULE® Glass for 4 decades:
  - A high-purity, single-phase SiO_2 glass doped with TiO_2
  - Used as a substrate for high performance mirrors:

Hubble Telescope
2.4 m Primary Mirror
(1978)

Subaru Telescope
8.2 m Primary Mirror
(1994)

- EUV Lithography driving material improvements:
  - "Polishability"
  - Absolute CTE better than ±5 ppb/K
  - Detailed metrology and uniformity requirements
  - Push for lower thermal expansion

Introduction – ULE® Glass (continued)

- Most outstanding feature of ULE® Glass is its extremely low coefficient of thermal expansion:
  - Mean $CTE_{5\text{-}35C}$ = 0±30 pp**b**/K (more than 100x better than PYREX®)

- Single-Phase Glass enables other important properties:
  - Long Term Dimensional stability

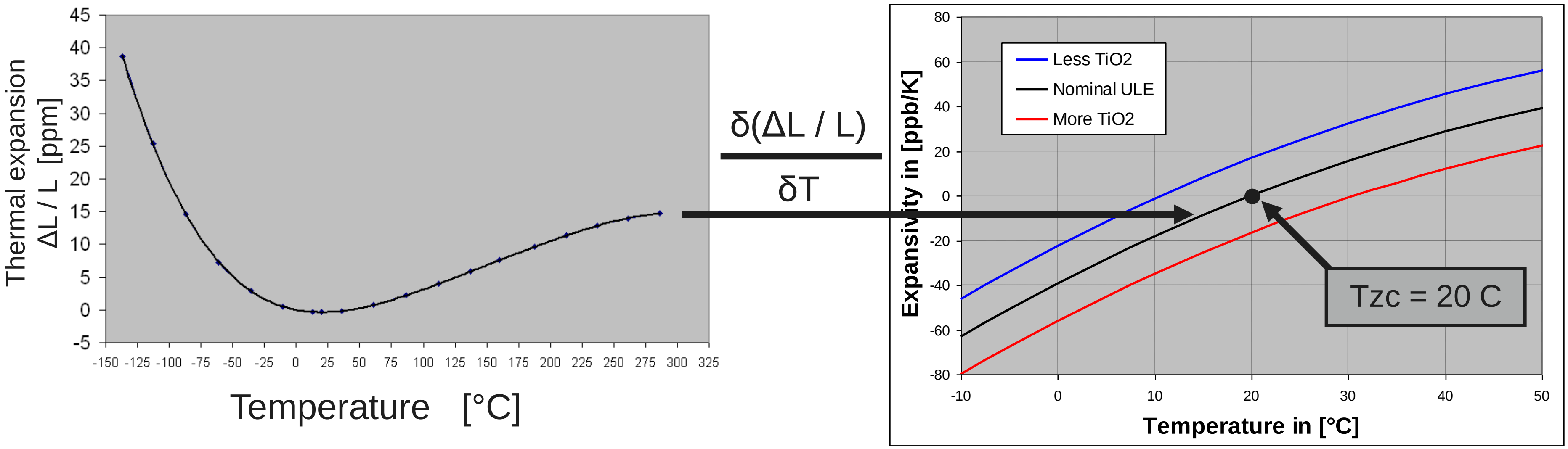
  - No hysteresis when cycled up to ~300 °C
    - Room-Temperature shape and CTE are unchanged
    - No specific thermal cycle or cooling rate is needed
    - No temporal drift in properties is triggered
    - Material is not affected by standard optical manufacturing and coating techniques

  - Mechanical strength
    - No delayed elastic effects have been observed (J.W. Pepi & D. Golini, Adv. Optics **20**, 3087 (1991)

ULE® Glass for EUVL – Why?

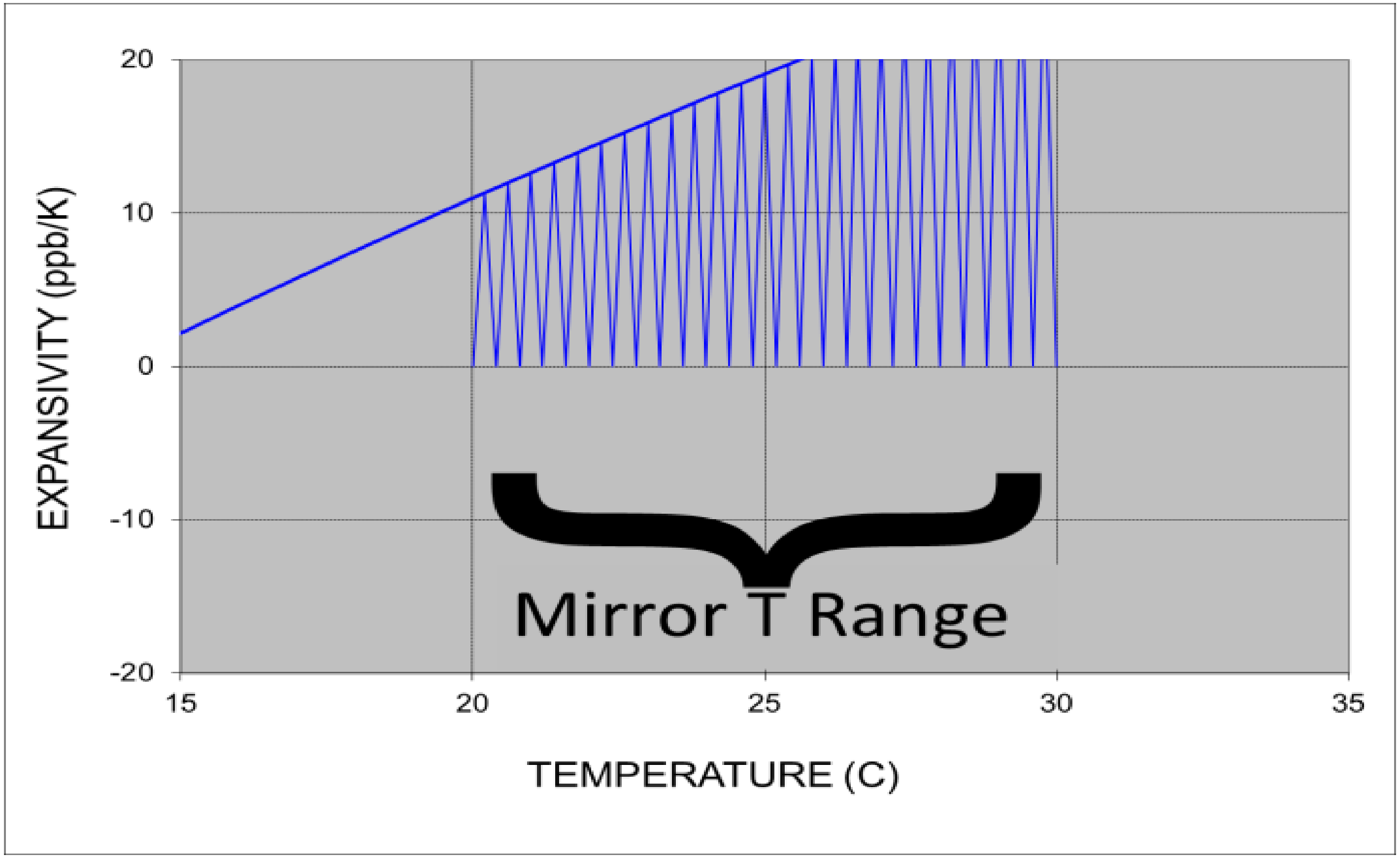
- High throughput in EUVL requires a bright light source (100's of Watts).
- Mirrors are expected to heat up:
  - Single mirror reflectivity is only ~70% at 13.5 nm.
  - Vacuum makes heat removal difficult.
  - In a 6 mirror + mask system, >90% of the light is absorbed before it gets to the wafer.
  - Ultra low expansion material in mask and mirrors is a must in order to preserve sub-nm wavefront distortion.
- ULE® Glass can be polished to sub nm roughness.
- Temperature of CTE=0 (crossover temperature T_{zc}) can be tuned.
- Metrology capable of non-destructively certifying material compliance within a narrow range.

Thermal Expansion in ULE® Glass



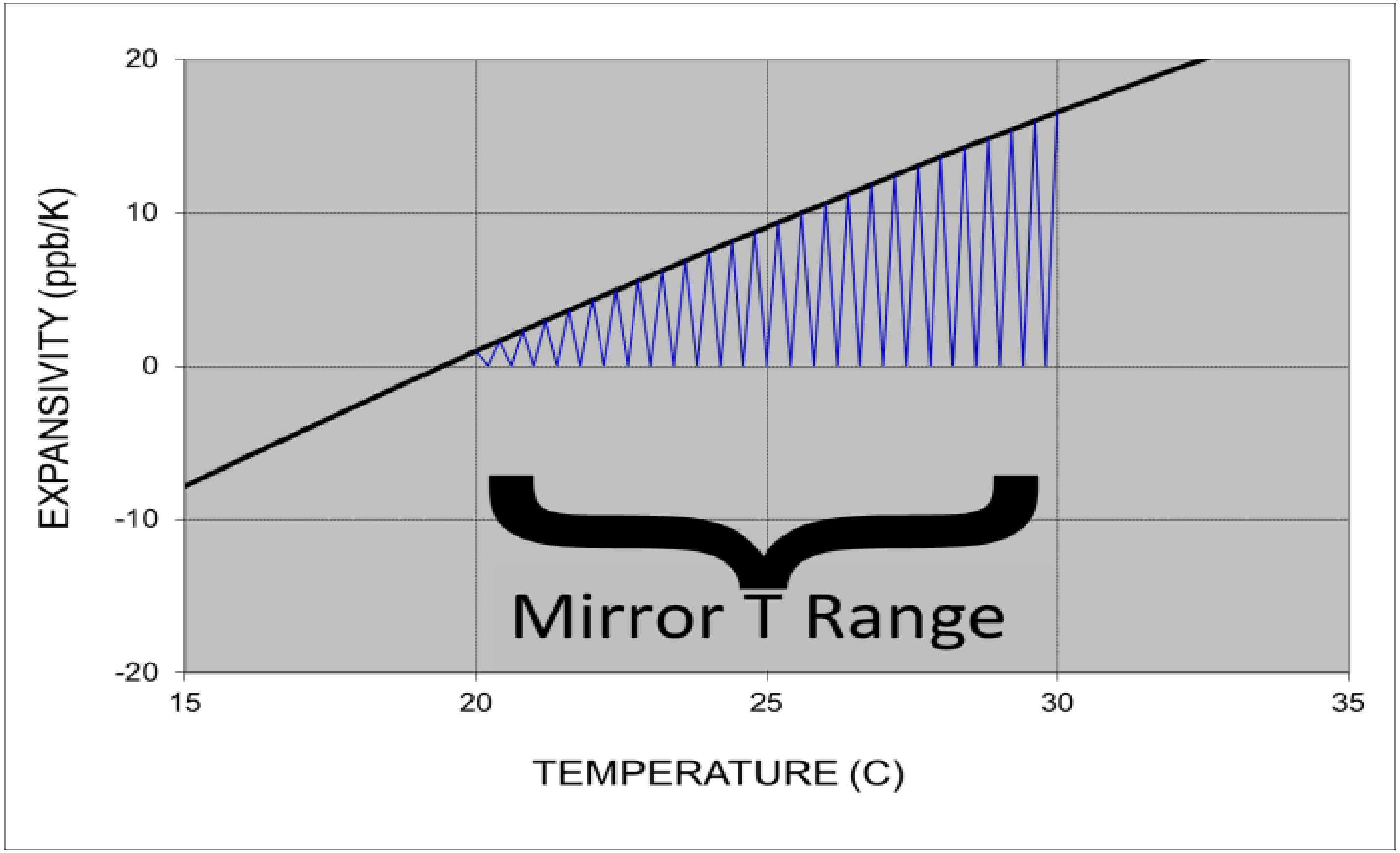
- CTE in ULE® Glass is controlled by composition:
  - Temperature dependence of expansivity curve is known.
  - Curve shifts in a predictable manner with changes in TiO_2 concentration.
  - Manufacturing adjustments in a narrow range around room temperature are understood, and compatible with production process.
  - Non-destructive metrology allows us to define the actual CTE of all glass we make (ultrasound velocity technique).

Minimizing Distortion in EUVL Optics and Masks



CASE I
Standard Grade
ULE® Glass

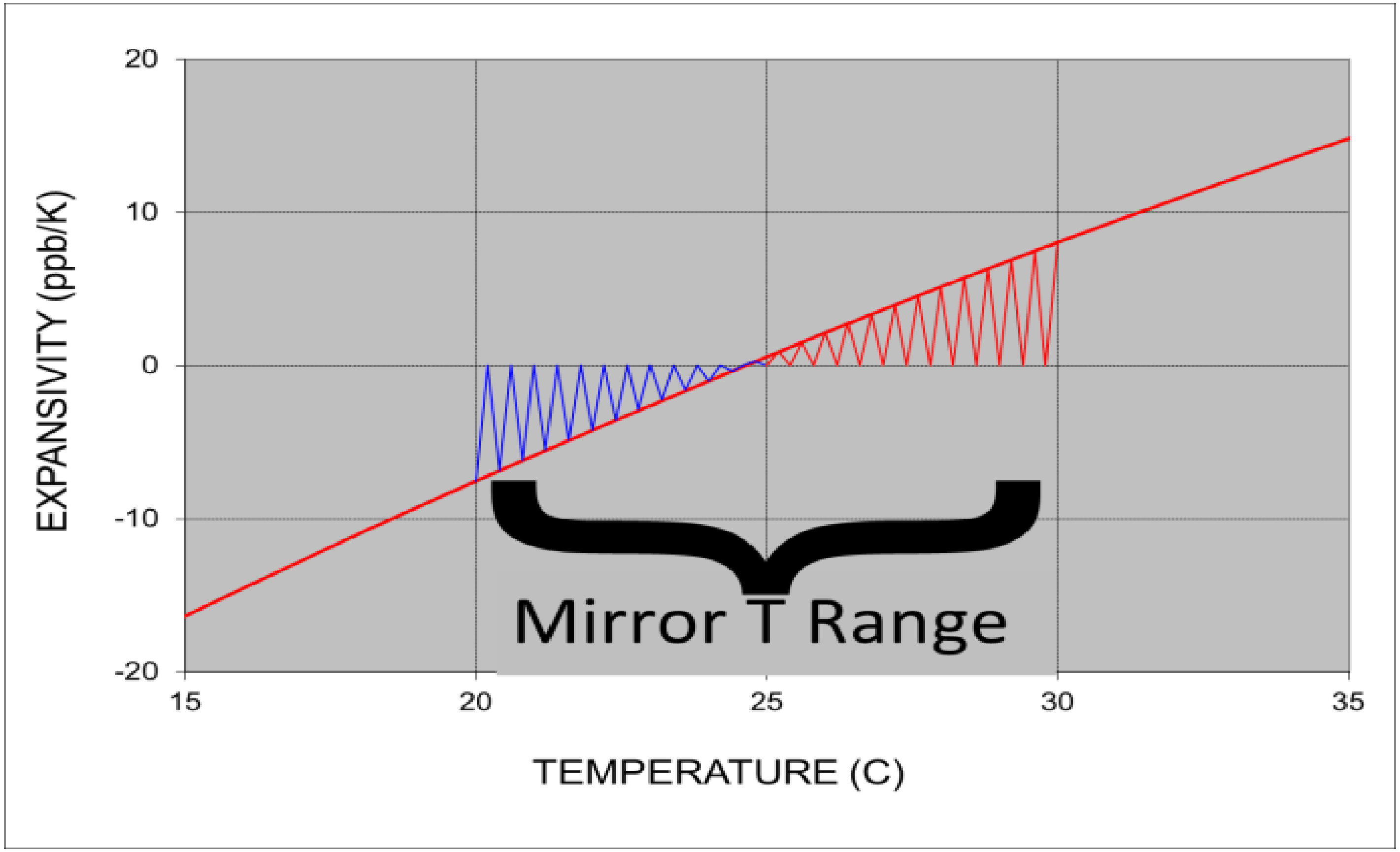
Minimizing Distortion in EUVL Optics and Masks



Case II
EUVL Grade
ULE®Glass
With T_{ZC} set at
~20ºC.

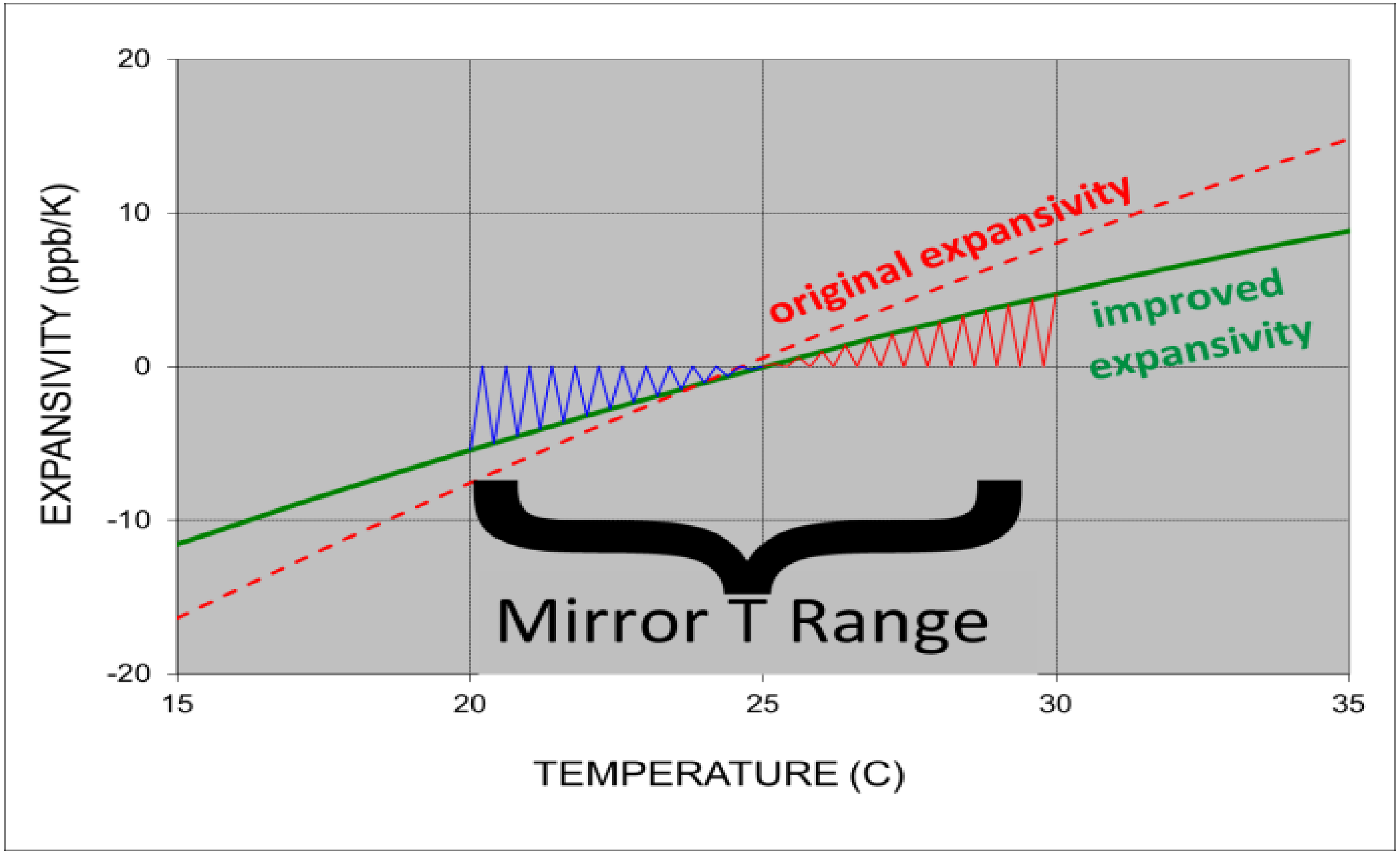
- Tune T_{zc} to expected temperature range in the optic:
  - Done by adjusting TiO_2 content during glass forming.
  - It is difficult to control when T_{zc} is tightly specified.

Minimizing Distortion in EUVL Optics and Masks



Case III
EUVL Grade
ULE® Glass.
With T_{ZC} set at
~midpoint.

Minimizing Distortion in EUVL Optics and Masks



Case IV EUVL Grade ULE®Glass.

With T_{ZC} set at ~midpoint.

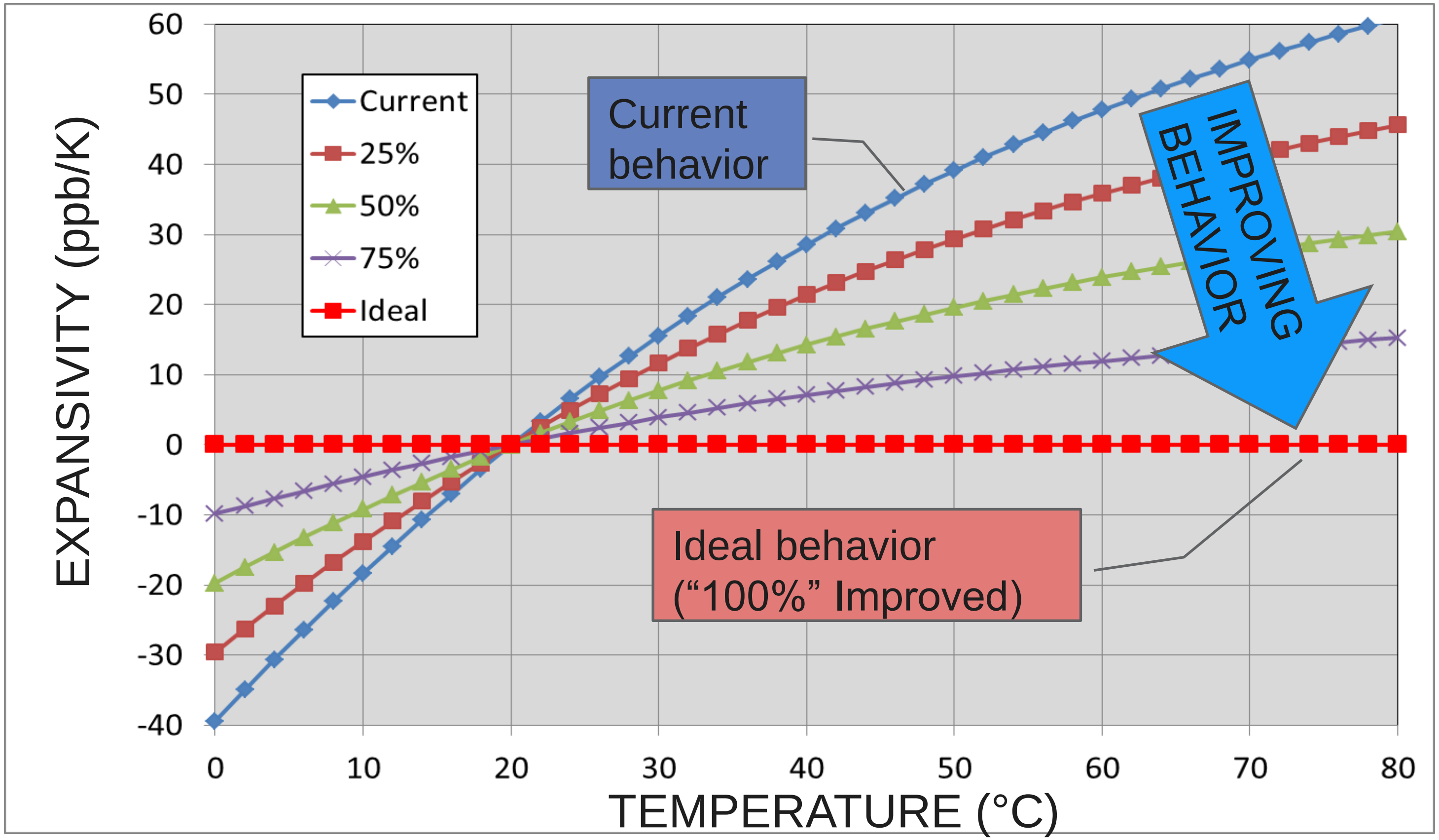
And

Reduced expansivity slope.

•Reduce slope of expansivity curve:

- In addition to tuning T_{zc}
- Gain becomes more important as the optic temperature range grows.

Expansivity Improvement Definition



Goal of this project was to optimize the expansivity through thermal treatment only, without introducing changes to a well established ULE® Glass production process.

Expansivity Improvement – Required Metrology

- Characterization of glass structural state after annealing:
  - We use Fictive Temperature (T_f) as parameter to describe the structural state of the glass.
  - Measure T_f through FTIR measurements (method by A. Agarwal, K.M. Davis and M. Tomozawa, J. Non-Crystalline Solids 185 (1995), p191-198). (J.E. Shelby, Phys. Chem. Glasses., 2005, 46 (5), 494-499).
  - Specific implementation and calibration for ULE® Glass submitted to J. Non-Crystalline Solids – Tingley et al. (2012).

- Measurement of effect on expansivity:
  - Sandwich Seal measurements

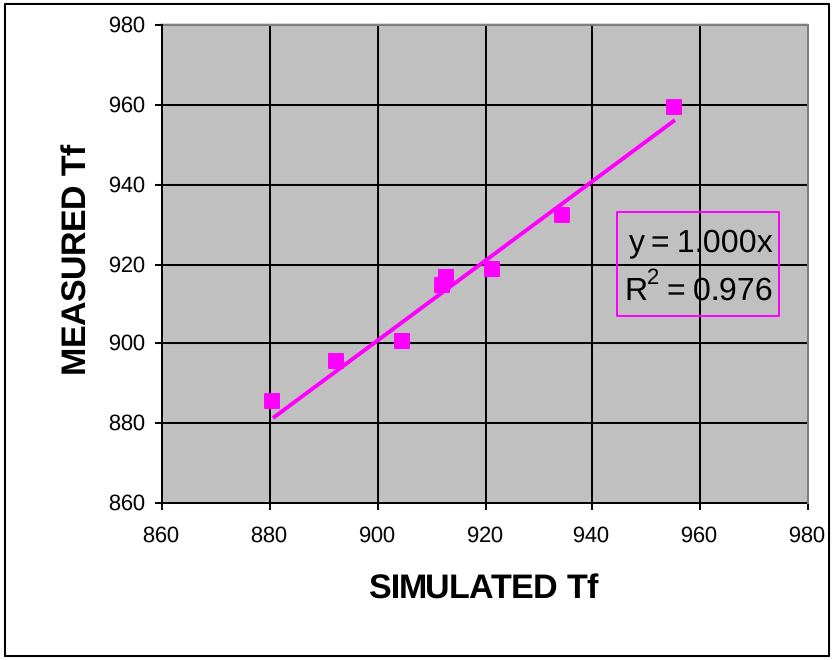
- Other production-compatible techniques
  - Modeling of T_f
  - Calibration of Ultrasound Velocity technique for improved material.

Glass T_f Characterization
FTIR Measurements and Empirical Modeling

- Quenched samples after isothermal holds at various temperatures to calibrate T_f vs. FTIR Peak Position.

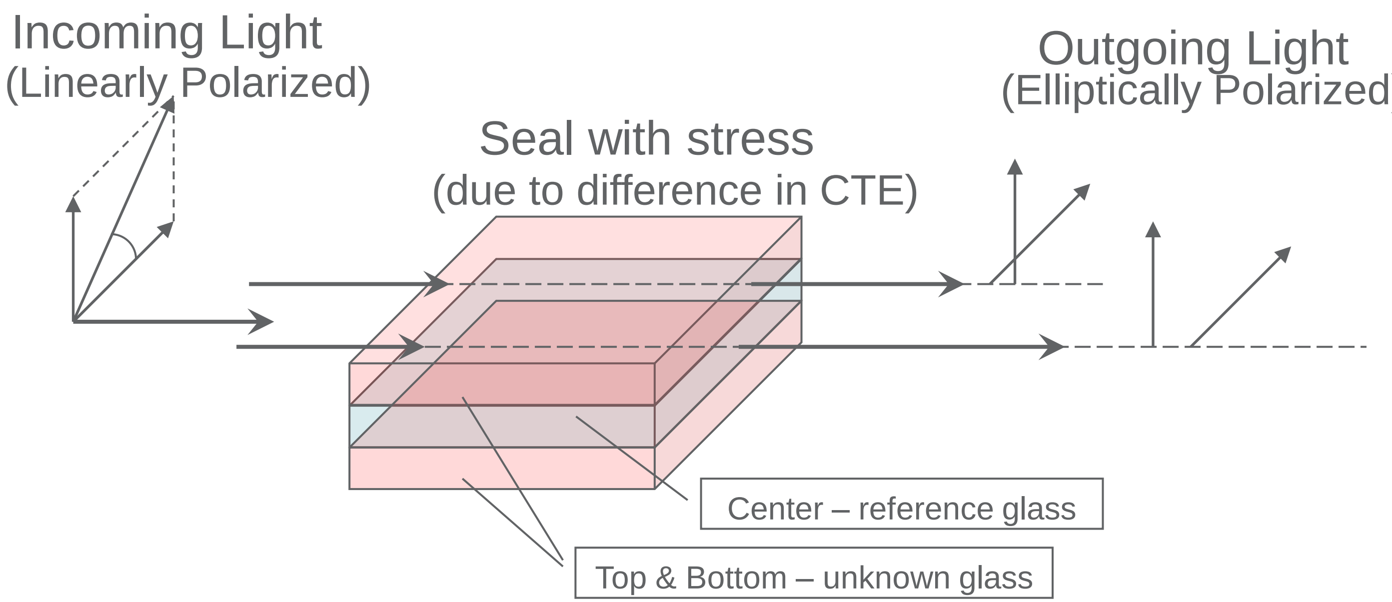
- Empirical model to calculate T_f after anneal and obtain correlation between model predictions and measurements.

Model Predictions vs. Measurements



Measuring Changes in Expansivity

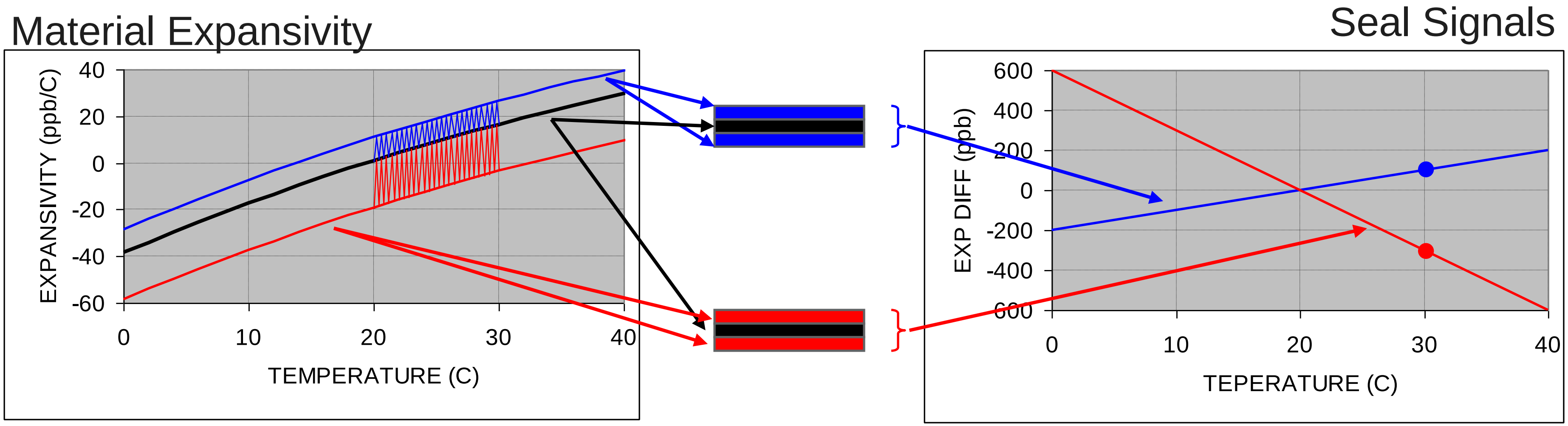
-Sandwich Seal Differential Expansion Measurement



- Use polarized light to measure stress, and evaluate thermal expansion.
- Technique by H. Hagy and collaborators, J. Opt. Soc. Am. **A3**, P83 (1986), and references therein.
- New setup incorporates computer control and data analysis:
  - Can detect small differences in thermal expansion.
  - Requires smaller samples than other techniques.
  - Temperature range from ~200 to 425 K (-70 to 150 °C).

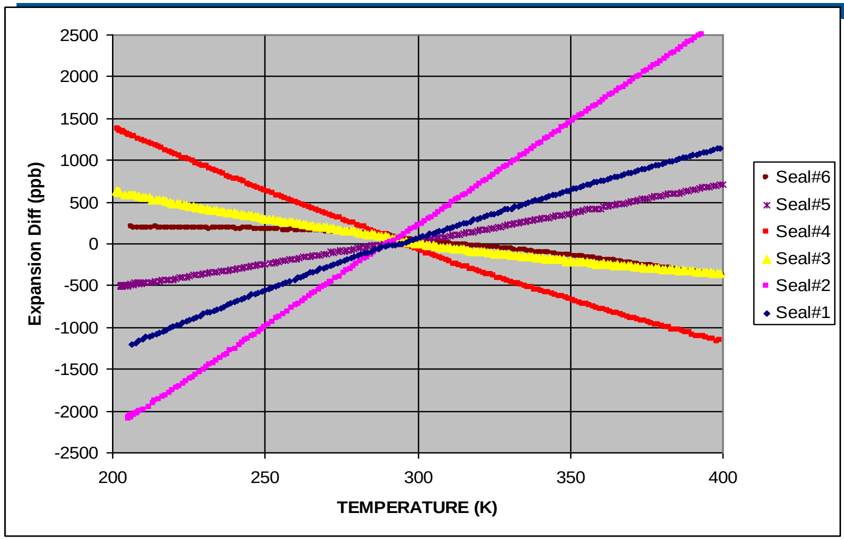
Sandwich Seal Data Analysis (Conceptual)

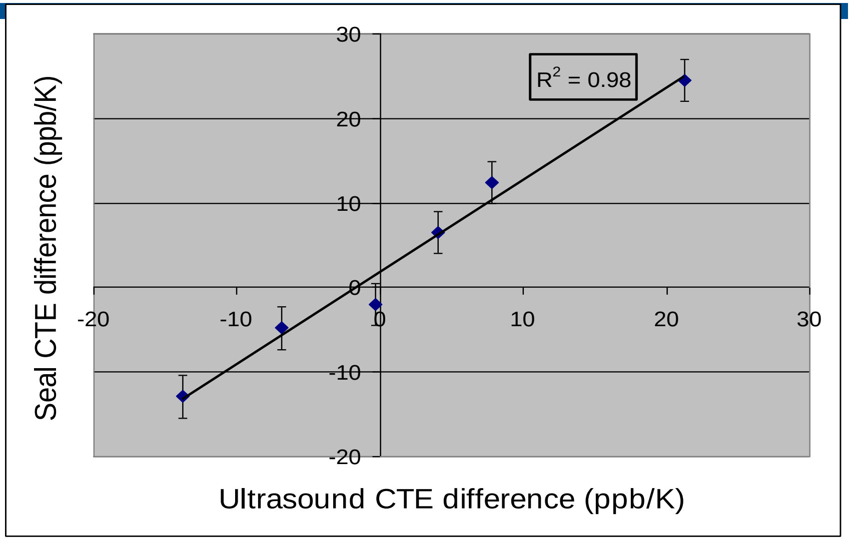
- Seals made with standard production ULE® Glass -



- Expansivity curves in production ULE® Glass have a constant shape vs. T
- Only effect of changes in TiO_2 concentration is to shift the curves vertically.
- Stress measured in sandwich seals made with this glass will be linear:
  - Sign of stress indicates whether “bread” expands more or less than “meat”.
  - Slope is a direct measurement of difference in CTE between bread and meat.

Sandwich Seal – Correlation to Ultrasound (Actual Measurements)

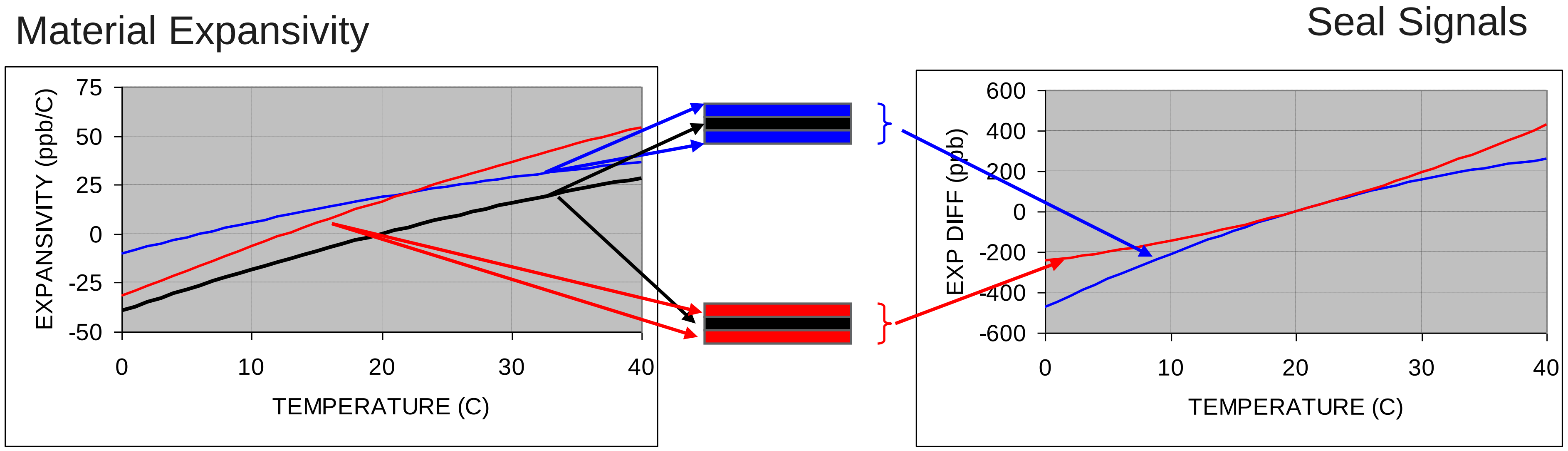




- Set of six sandwich seal samples were made using ULE® Glass with different amounts of TiO_2 doping.
- System has excellent sensitivity to small expansion differences.
- Expansion Difference vs. Temperature plots are straight lines:
  - Explicitly shows that Expansivity is independent of CTE offset.
- Uncertainty in CTE difference from Sandwich Seal is ~±2-3ppb/K
  - Excellent tool for evaluation of new materials.

Sandwich Seal Data Analysis (Conceptual)

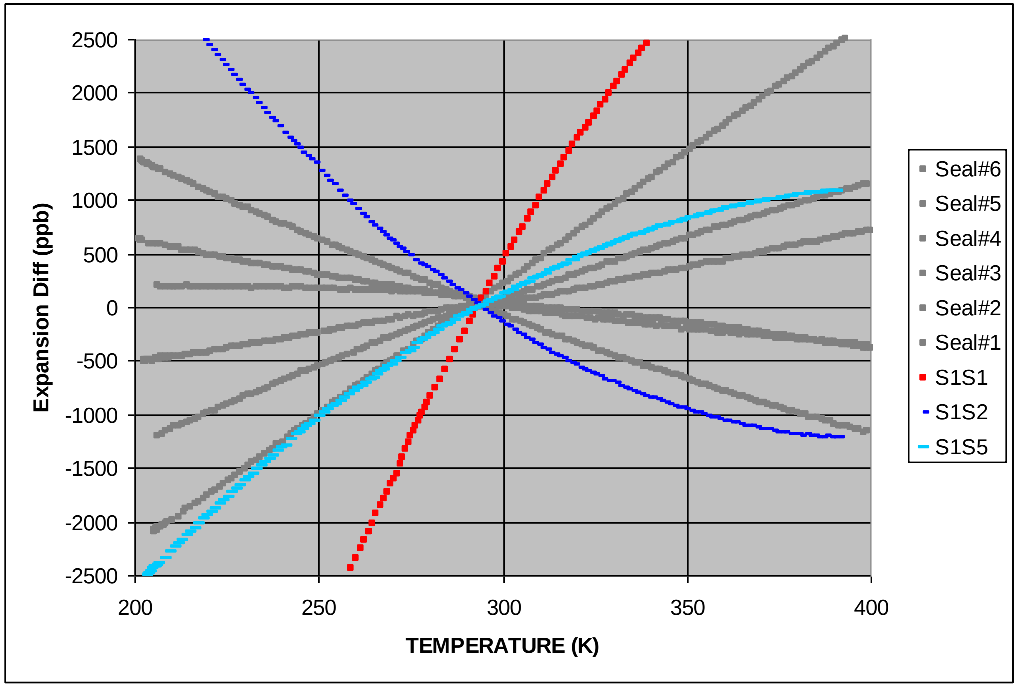
- Seals made with non-Standard ULE® Glass -



- Seals are prepared using Standard ULE® Glass for the "meat", and non-standard for the "bread"
- If expansivity curves are not parallel, measured stress is no longer linear with temperature.
- Fit measured seal stress adding a quadratic term:
  - Sign and magnitude of quadratic term indicates whether the bread expands slower than or faster than standard ULE® Glass.

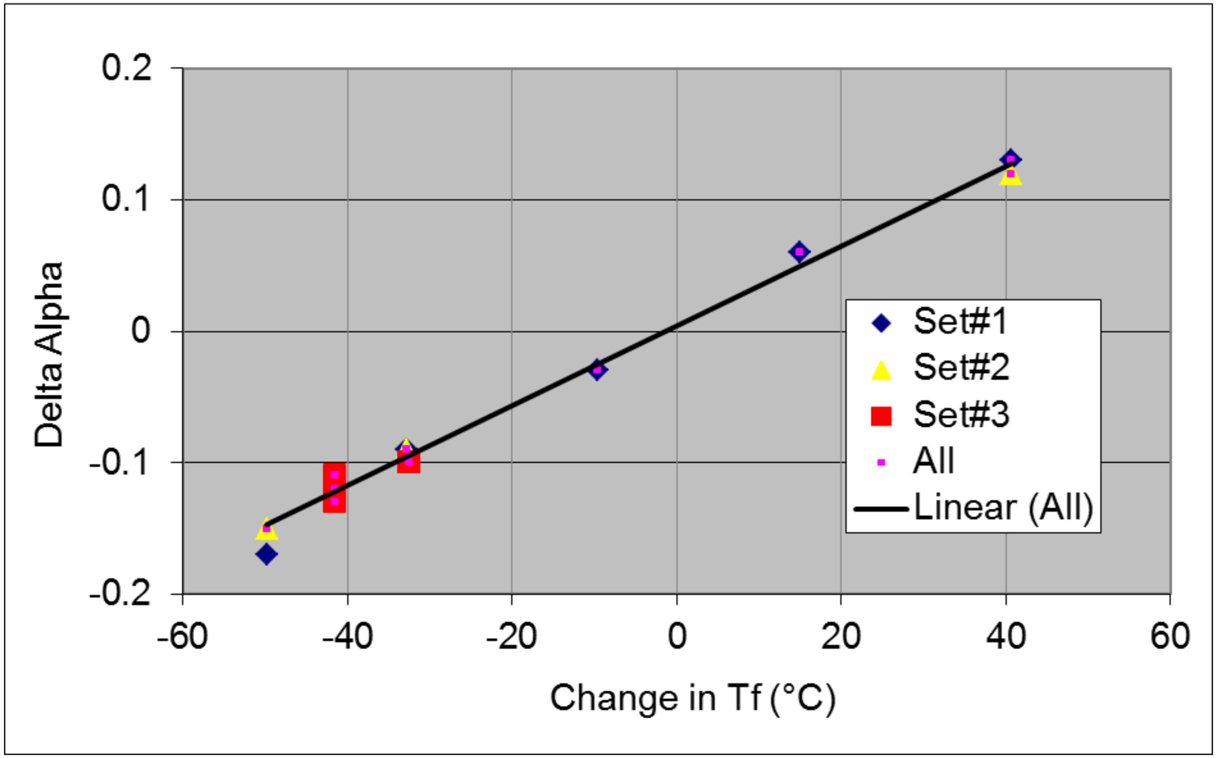
Sandwich Seal Measurement Results (Actual Measurements)

Seals made with “bread” slices of non-Std Anneal ULE®



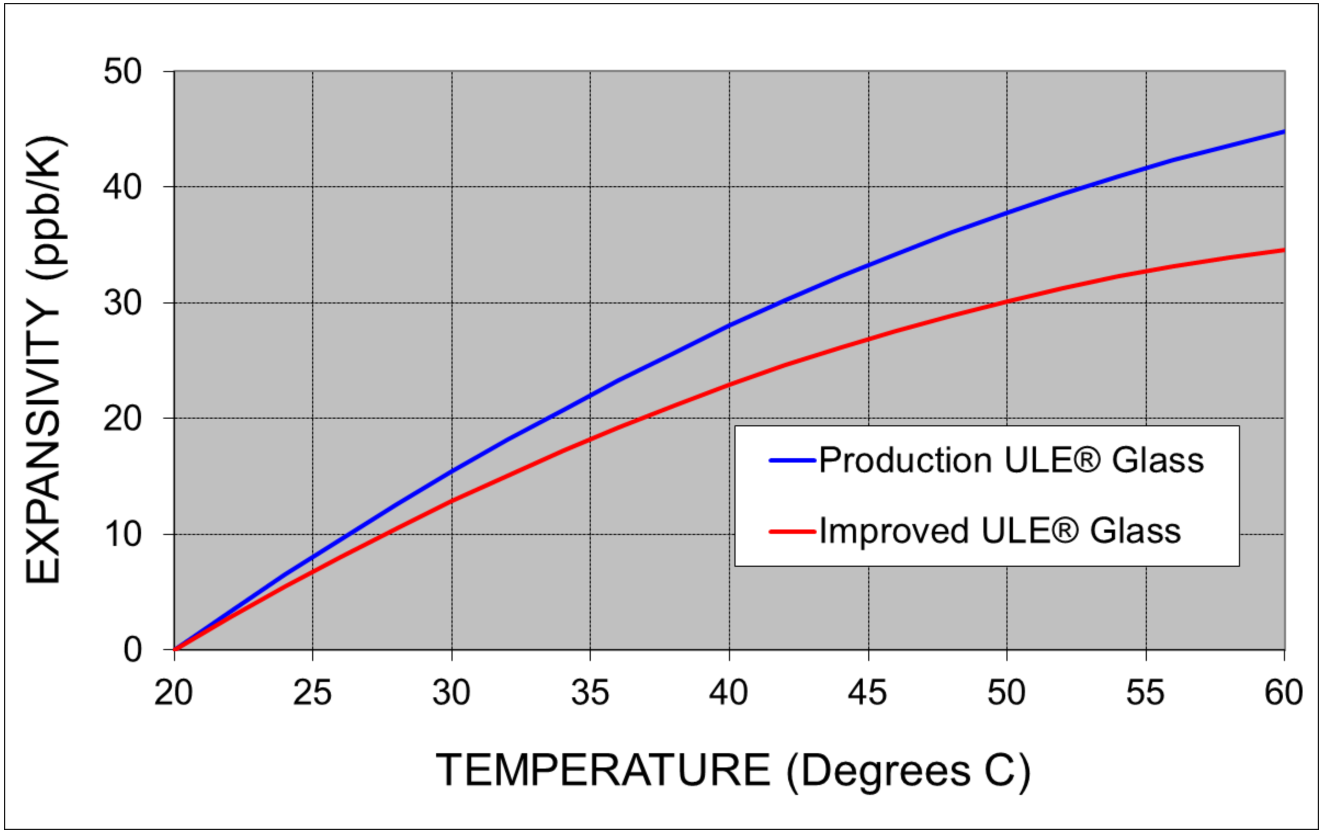
- Curved lines indicate expansivity slope change.
- Measurement of curvature allows quantification of improvements in expansivity (next slide).

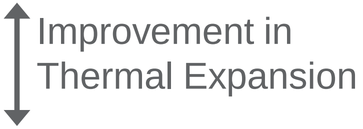
Change in Expansivity Slope (Quadratic Term in Sandwich Seal Fits)



- Samples prepared from different Boules of ULE® Glass.
- Consistent behavior seen for all seals measured.
- US Patent Applications 2011/0207592 and 2011/0207593

Thermal Expansion in Improved ULE® Glass





- Improvement shown in this figure is ~ 24%
- US Patent Applications 2011/0207592 and 2011/0207593

Summary

- Until now, T_{zc} of ULE® Glass has been determined during the glass forming process

- Using controlled annealing, we can simultaneously improve the expansivity and fine tune the T_{zc} of ULE® Glass (US Patent Application 2011/0048075)
  - Process can be tuned to meet specific customer requirements.
  - We have demonstrated improvements in expansivity greater than 30%.
  - T_{zc} tuning will allow us to supply glass within narrower specification ranges

- Corning ULE® Glass is an enabler for EUV Lithography today
  - We are committed to continue to improve material properties and manufacturing processes towards future needs

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